



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 1/14, 17/06, 11/02	A1	(11) International Publication Number: WO 93/02168 (43) International Publication Date: 4 February 1993 (04.02.93)
(21) International Application Number: PCT/US92/05659 (22) International Filing Date: 6 July 1992 (06.07.92) (30) Priority data: 730,155 15 July 1991 (15.07.91) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: KAMINSKY, George, John ; 1612 Peaslee Avenue, Cincinnati, OH 45224 (US). MUELLER, Frank, Joseph ; 218 Solarama Court, Cincinnati, OH 45238 (US). (74) Agent: REED, T., David; The Procter & Gamble Company, Ivorydale Technical Ctr., 5299 Spring Grove Ave., Cincinnati, OH 45217-1087 (US).		(81) Designated States: AU, BB, BG, BR, CA, CS, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR PRODUCING A DETERGENT COMPOSITION CONTAINING ALKYL SULFATE PARTICLES AND BASE GRANULES (57) Abstract This relates to a process for the production of a granular detergent composition comprising admixed high active alkyl sulfate particles made by steps including continuous neutralization, and spray dried granules comprising detergency builder, soluble silicate, and essentially no alkyl sulfate.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

PROCESS FOR PRODUCING A DETERGENT COMPOSITION CONTAINING ALKYL
SULFATE PARTICLES AND BASE GRANULES

FIELD OF THE INVENTION

The present invention relates to a process for preparing granular detergent compositions by separately preparing spray dried base granules and alkyl sulfate particles, and then admixing them.

BACKGROUND OF THE INVENTION

The traditional method for producing detergent granules is spray drying. Typically, detergent ingredients such as surfactant, builder, silicate and carbonate are mixed in a tank to form a slurry which is about 35% to 50% water. This slurry is then atomized in a spray drying tower to reduce moisture. It is possible to compact spray dried particles to make dense detergent granules. See U.S. Patent 4,715,979, Moore et al., issued December 29, 1987. However, spray drying methods generally involve a limited amount (less than 40%) of organic components such as surfactant for environmental and safety reasons.

An alternative method for making detergent particles is by continuous neutralization in, for example, a continuous neutralization loop, followed by particle formation. Copending U.S. Patent Application Serial No. 647,338, Mueller et al, filed January 28, 1991, which is a continuation-in-part of Serial No. 364,721, filed June 9, 1989, describes the formation of high active (>50% active) detergent granules using a continuous neutralization system followed by particle formation. Polyethylene glycol and/or certain ethoxylated nonionic surfactants are added during neutralization of alkyl sulfuric and/or alkyl benzene sulfonic acids with concentrated sodium hydroxide (\geq about 62%). The process and particles made by the process are included. This case published as EP 90 306 139.8 on December 12, 1990.

Copending U.S. Patent Application Serial No. 552,663, Ofosu-Asante et al, filed July 16, 1990 (allowed), describes a process for producing high active detergent particles which

SUBSTITUTE SHEET

- 2 -

includes reacting in a continuous neutralization system the acid form of an anionic surfactant with alkali metal hydroxide and adding to the neutralization system during formation of the neutralized product an α -aminodicarboxylic acid selected from the group consisting of glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid, and 2-amino-2-methylpentanedioic acid, or their alkali metal salts. High active detergent particles are included.

Copending U.S. Patent Application Serial No. 288,759, Strauss et al, filed December 22, 1988 (allowed), describes a process for preparing concentrated surfactant granules from a high active surfactant paste using fine dispersion cold granulation. This published as EP 89 306 335.4 on January 3, 1990.

U.S. Patent 4,534,879, Iding et al, issued August 13, 1985, discloses a process for making improved synthetic surfactant flakes from a roll drum dried paste containing sodium alkyl sulfate, sodium alkylbenzene sulfonate, and water-soluble inorganic salts. The hot flakes are cooled in a low moisture environment having a low dew point.

None of the above disclose the instant process for producing a granular detergent composition by admixing high active alkyl sulfate particles with spray dried base granules containing little to no alkyl sulfate, nor do they disclose a composition comprising particles with high levels of alkyl sulfate, and C₁₀-16 linear alkylbenzene sulfonate and/or C₁₂-18 soap, along with granules containing detergency builder and soluble silicate, which are essentially free of alkyl sulfate.

SUMMARY OF THE INVENTION

The present invention relates to a process for the production of a granular detergent composition, comprising:

- (a) spray drying a slurry comprising, by weight of the spray dried granules: less than about 2% of alkyl sulfate; from 0 to about 40% of anionic surfactant other than

- 3 -

alkyl sulfate; from about 10 to 80% of detergency builder; and from about 1 to 15% of soluble silicate;

- (b) producing alkyl sulfate particles by steps comprising continuous high active neutralization, said particles comprising, by weight of the alkyl sulfate particles: from about 60 to 99% of C₁₂₋₁₈ alkyl sulfate ethoxylated with from 0 to about 4 moles of ethylene oxide per mole of alkyl sulfate; and
- (c) admixing said spray dried granules with said alkyl sulfate particles, respectively, in a ratio between about 10:90 and 99:1.

DESCRIPTION OF THE INVENTION

As an effort initially to reduce plume emission from the spray drying tower and improve physical properties of high surfactant spray dried particles, alkyl sulfate was removed from the spray drying process and included in a separately made "alkyl sulfate particle". It has been found that removal of the alkyl sulfate from the spray drying tower reduces the total amount of sticky organic material in spray dried "base granules", thus improving lumping and caking properties. It has also been found that adding the alkyl sulfate outside the spray drying tower via a separate process reduces the total organic load in the tower, thus reducing visible plume and reducing environmental impact.

It has further been found that production rates for nil-P (no phosphate) granules can be increased (up to about 30%; based on equivalent tower drying loads and crutcher moistures) if the alkyl sulfate is added as a separate particle.

It is believed that removal of the other predominant, frequently-used anionic surfactant, linear alkylbenzene sulfonate ("LAS"), from the spray drying tower alone does not result in plume reduction as does alkyl sulfate.

Production of alkyl sulfate particles by continuous neutralization is described in Copending U.S. Patent Application Serial Numbers 647,338 and 552,663 cited above.

- 4 -

In this process, spray dried granules are made by conventional spray drying means. They are comprised of less than about 2% alkyl sulfate, detergency builder, and soluble silicate. Other detergent ingredients conventionally added into spray dried granules may also be added here. Alkyl sulfate particles are made in a separate process using a continuous high active neutralization system (see below). The spray dried granules are then admixed with the alkyl sulfate particles. Other conventional detergent ingredients may also be admixed.

A consumer acceptable product which can be made with less plume emission, higher production rates, and improved physical properties is achievable using this invention. Also, surfactant levels in a detergent composition can be easily increased by adding more alkyl sulfate particles to the composition. High density granular detergent compositions are more easily made because of the flexibility of mixing the alkyl sulfate particles. Detergency builder, soluble silicate, anionic surfactant, and other desired ingredients can be added via the spray dried granules, and higher levels of the alkyl sulfate, which are difficult to put into the spray dried granules, can be added via the alkyl sulfate particles.

The term particles is used interchangeably with granules herein.

I. Alkyl Sulfate Particles

Alkyl sulfate particles are produced by steps comprising continuous high active neutralization. These particles are comprised of, by weight of the alkyl sulfate particles, from about 60 to 99%, preferably about 70 to 90%, of C₁₂₋₁₈, preferably C₁₄₋₁₆, alkyl sulfate ethoxylated with from 0 to about 4 moles of ethylene oxide per mole of alkyl sulfate. The alkyl sulfate is preferably not ethoxylated (0 moles of ethylene oxide). It is preferred that the alkyl sulfate particles contain from about 4 to 25%, preferably about 8 to 14%, by weight of the alkyl sulfate particles, of C₁₀₋₁₆, preferably C₁₁₋₁₄, linear alkylbenzene

- 5 -

sulfonate, especially where nonethoxylated alkyl sulfate is used. Mixtures of alkyl sulfate and alkyl ethoxy sulfate may be used. Where alkyl ethoxy sulfate is used, from about 0.5 to 2 moles of ethylene oxide per mole of alkyl sulfate is preferred. Alkyl sulfate flakes are preferred.

Useful alkyl sulfate surfactants are the water soluble salts, particularly the alkali metal, ammonium and alkanolammonium (e.g., monoethanolammonium or triethanolammonium) salts of C₁₂-16 linear or branched alkyl sulfates.

The alkyl sulfate particle making process comprises the following steps.

A. Addition of Acid and Caustic

The first step of this process is reacting in a continuous neutralization system C₁₂-18 alkyl (ethoxylated) sulfuric acid, and preferably C₁₀-16 alkyl benzene sulfonic acid or mixtures thereof, with a sodium hydroxide solution, which is greater than or equal to about 62% by weight of the hydroxide, preferably without kneading, to produce a neutralized product. The neutralized product preferably has less than or equal to about 12% by weight of water.

It is preferred that the materials of the detergent composition not be kneaded in the continuous neutralization system. The continuous neutralization system preferably does not include an airtight-type kneader.

It is preferred that the continuous neutralization system be substantially free of additional crude materials of the detergent composition. In other words, crude materials other than surfactant, caustic and/or polyethylene glycol are preferably not fed into the system. For example, less than about 5%, preferably less than about 1%, of additional crude materials should be present in the continuous neutralization system. It is most preferred that essentially no detergency builders or additional organic materials are fed into the continuous neutralization system.

- 6 -

The C₁₂₋₁₈ alkyl (ethoxylated) sulfuric acid and C₁₀₋₁₆ alkyl benzene sulfonic acid can be made by any sulfation/sulfonation process, but preferably are sulfonated with SO₃ in air in a falling film reactor. See Synthetic Detergents, 7th ed., A.S. Davidson & B. Milwidsky, John Wiley & Sons, Inc., 1987, pp. 151-168.

C₁₂₋₁₈ alkyl sulfuric acid, and mixtures of it and C₁₀₋₁₆ linear alkyl benzene sulfonic acid, are preferred for use herein. Mixtures of the two are most preferred because of improved dispersibility of detergent particles formed from a paste made with the mixture. The two acids can be added as separate streams to the continuous neutralization system or mixed before addition. Alternatively, pastes made from each separate acid can be mixed after neutralization.

In this process, it is preferred that the final ratio of C₁₂₋₁₈ sodium alkyl sulfate to C₁₀₋₁₆ sodium linear alkyl benzene sulfonate be between 75:25 and 96:4, preferably between 80:20 and 95:5.

C₁₄₋₁₆ alkyl sulfuric acid is preferred for use in step (a) of this process over C₁₂₋₁₈ alkyl sulfuric acid. C₁₄₋₁₅ alkyl sulfuric acid is most preferred.

C₁₁₋₁₄ linear alkyl benzene sulfonic acid is preferred over C₁₀₋₁₆ alkyl benzene sulfonic acid. C₁₂₋₁₃ linear alkyl benzene sulfonic acid is most preferred for use herein.

The sodium hydroxide used in step (a) to neutralize the alkyl sulfuric acid and/or alkyl benzene sulfonic acid is greater than or equal to about 62%, preferably greater than or equal to about 68%, most preferably about 73%, by weight of the hydroxide. This highly concentrated caustic solution melts at a high temperature so the caustic feed system must be carefully maintained at the required temperature to prevent "cold spots". A "cold spot" is any point in the feed system, pumps, metering systems, pipes or valves where the system has reached a temperature below the melting point of the caustic (155°F or 68.3°C for 73% caustic, for

35

- 7 -

example). Such a "cold spot" can cause crystallization of the caustic and blockage of the feed system. Typically "cold spots" are avoided by hot water jackets, electrical tracing, and electrically heated enclosures.

5 The sodium hydroxide is preferably present in slight excess of the stoichiometric amount necessary to neutralize the acid. If excess alkalinity (excess caustic) in the neutralization system exceeds about 1.5% M_2O (where M is metal), the paste is difficult to circulate through the continuous neutralization system because
10 of its high viscosity. If excess alkalinity drops below about 0.1%, the alkyl paste may not be stable long term because of hydrolysis. It is therefore preferred that excess alkalinity, which can be measured by titration with acid, of the molten paste in the neutralization system be between about 0.1% and 1.5%, more
15 preferably between about 0.2% and 1.0%, most preferably between about 0.3% and 0.7%.

 The acid and caustic are put into the continuous neutralization system separately, preferably via a high shear mixer so that they mix together as rapidly as possible. The high shear mixer is
20 preferably specifically designed for complete mixing of viscous liquids.

 Generally, in a continuous neutralization loop, the ingredients enter the system through a pump (typically centrifugal) which circulates the material through a heat
25 exchanger in the loop and back through the pump, where new materials are introduced. The material in the system continually recirculates, with as much product exiting as is entering. Product exits through a control valve which is usually after the pump. The recirculation ratio of a continuous neutralization loop
30 is between about 1:1 and 50:1. The temperature of the neutralization reaction can be controlled somewhat by adjusting the amount of cooling by the heat exchanger. The "throughput" can be controlled by modifying the amount of acid and caustic introduced.

- 8 -

The continuous neutralization loop should be modified as follows to practice this process:

- (1) Insulate the loop;
- (2) Change the centrifugal pump to a positive displacement pump, which is better able to handle very viscous material;
- (3) Install a caustic feed system which can handle concentrated caustic (greater than about 50% solids);
- (4) Introduce materials through a high shear mixer installed in-line;
- (5) Install a metering system for the polyethylene glycol and/or ethoxylated nonionic surfactant, preferably after the high shear mixer; and
- (6) Position the incoming streams of acid and caustic at the high shear mixer so that the highest degree of mixing possible takes place.
- (7) The temperature of the loop should be sufficiently high to achieve a low viscosity of the paste to ensure adequate recirculation and mixing. The temperature should not be so high however that it causes hydrolysis of the alkyl sulfuric acid or the alkyl sulfate. Typical paste temperatures in the loop are between about 180°F (82.2°C) and 230°F (110°C), preferably about 200°F (93.3°C) to 210°F (98.9°C).

B. Addition of Polyethylene Glycol and/or Ethoxylated Nonionic Surfactant

An optional second step of this process is adding to the continuous neutralization system during formation of the neutralized product polyethylene glycol of a molecular weight between about 2,000 and 50,000 and/or ethoxylated nonionic surfactant of the formula $R(OC_2H_4)_nOH$, wherein R is a C₁₂₋₁₈ alkyl group or a C₈₋₁₆ alkyl phenol group and n is from about 9 to about 80, with a melting point greater than or equal to about 120°F

35

- 9 -

(48.9°C). The weight ratio of the additive of step (b) to the mixture of step (a) is from about 1:5 to about 1:20.

The polyethylene glycol and/or the ethoxylated nonionic surfactant can be added separately or as a mixture to the continuous neutralization system at any point. In a neutralization loop, these additive(s) preferably enter the loop after the high shear mixer and before the recirculation pump. The additives must be melted before addition to the neutralization system, so that they can be metered in.

These two additives are chosen because they enhance detergent performance and are solid at below about 120°F (48.9°C), so that a detergent particle which is firm at ambient temperature can be made from the neutralized paste. They are also chosen because each additive acts as a process aid by reducing the viscosity of the high active paste in the neutralizer loop. This viscosity reduction is particularly important during the start up of the neutralizer loop where the surfactant concentration is increased through the "middle phase" region. Some alkyl sulfate chain lengths have very high "middle phase" viscosities - typically between concentrations of 40% and 60%.

Polyethylene glycol of a molecular weight between about 2,000 and 50,000 is preferred over the ethoxylated nonionic surfactants. Polyethylene glycol of a molecular weight between about 3,000 and 20,000, preferably 7,000 and 12,000 is more preferred, and most preferred is polyethylene glycol with a molecular weight of 8,000 ("PEG 8,000"). In this invention, the preferred weight ratio of polyethylene glycol to the acid/caustic mixture of step (a) is from about 1:8 to about 1:12. For polyethylene glycol with a molecular weight of 8,000, the preferred weight ratio is one part PEG 8,000 to ten parts acid/caustic mixture.

Polyethylene glycol is formed by the polymerization of ethylene glycol with ethylene oxide in an amount sufficient to provide a compound with a molecular weight between about 2,000 and 50,000. It can be obtained from Union Carbide (Danbury, CT).

- 10 -

The preferred ethoxylated nonionic surfactant material is of the formula $R(OC_2H_4)_nOH$, wherein R is a C₁₂-18 alkyl group and n is from about 12 to about 30. Most preferred is tallow alcohol ethoxylated with 18 moles of ethylene oxide per mole of alcohol ("TAE 18"). The preferred melting point for the ethoxylated nonionic surfactant is greater than about 140°F (60°C).

Examples of other ethoxylated nonionics herein are the condensation products of one mole of decyl phenol with 9 moles of ethylene oxide, one mole of dodecyl phenol with 16 moles of ethylene oxide, one mole of tetradecyl phenol with 20 moles of ethylene oxide, or one mole of hexadecyl phenol with 30 moles of ethylene oxide.

Continuous neutralization can be conducted by a process comprising the steps of:

- (a) reacting in a high active continuous neutralization loop the acid form of said alkyl sulfate with sodium hydroxide solution, which is about 30 to 75% by weight of the hydroxide and is present in stoichiometric amount to slight stoichiometric excess, to produce a neutralized product;
- (b) adding to said continuous high active neutralization loop, during formation of said neutralized product, an α -aminodicarboxylic acid selected from the group consisting of glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid, and 2-amino-2-methyl-pentanedioic acid, or their alkali metal salts, such that particles formed from the product of step (b) are comprised of from about 0.2 to 15 weight % of the α -aminodicarboxylic acid salt.

An alkali metal salt of glutamic acid or aspartic acid is preferably added to the neutralization loop. Preferably, from about 1 to 10 weight % mono- and/or disodium glutamate is added to the neutralization loop.

- 11 -

The alkali metal hydroxide solution is preferably about 62 to 73% by weight of the hydroxide. Sodium hydroxide is preferred.

The neutralized product preferably has less than or equal to about 12% by weight of water.

5 C. Formation of Particles

The third step of this alkyl sulfate particle-making process is forming detergent particles. Detergent particles can be formed in various ways from the neutralized product exiting the continuous neutralization system. A desirable detergent particle
10 size distribution has a range of about 100 to 1200 microns, preferably about 150 to 600 microns, with an average of 300 microns.

The molten paste from a continuous neutralization loop can be atomized into droplets in a prilling (cooling) tower. To avoid
15 prilling at all, the molten paste can be simultaneously cooled and extruded, and cut or ground into desirable particle sizes.

A third choice is to allow the molten paste to cool on a chill roll, or any heat exchange unit until it reaches a doughy consistency, at which point other detergent ingredients can be
20 kneaded in. The resulting dough can then be granulated by mechanical means.

A fourth and preferred choice is to cool the molten paste into flakes on a chill roll, then grind the flakes to the desired particle size. If additional drying is required, the cooled
25 flakes can be dried in a rotary drum with hot air or in a fluid bed prior to grinding.

II. Spray Dried Granules

The spray dried granules for use in this process can be made by any conventional spray drying process. They are made by a
30 spray drying process comprising spray drying a slurry comprising, by weight of the spray dried granules: less than about 2% of alkyl sulfate; from 0 to about 40% of anionic surfactant other than alkyl sulfate; from about 10 to 80% of detergency builder; and

- 12 -

from about 1 to 15%, preferably 2 to 5%, of soluble silicate (as a structurant).

From about 5 to 30% of anionic surfactant is preferred. The anionic surfactant is preferably a salt of C₁₀₋₁₆ linear alkylbenzene sulfonate. From about 10 to 20% of sodium C₁₁₋₁₄ linear alkylbenzene sulfonate is most preferred.

Nil-P granules are preferred. The spray dried granules are preferably comprised of from about 30 to 60 weight % of detergency builder selected from the group consisting of carbonate, citrate, aluminosilicate, and mixtures thereof. Most preferably, from about 5 to 60 weight % of sodium carbonate and/or water-soluble inorganic salt, preferably sodium sulfate, is included.

In one embodiment, the spray dried granules are comprised of from about 5 to 50 weight % of sodium aluminosilicate.

Applicable spray drying processes are described in U.S. Patents 4,715,979, Moore et al, issued December 29, 1987, 4,963,226, Chamberlain, issued October 16, 1990, and 4,344,871, Allaway et al, issued August 17, 1982, which are incorporated herein by reference.

III. Admix

The spray dried granules and the alkyl sulfate particles are admixed, respectively, at a ratio between about 10:90 and 99:1, more preferably between about 50:50 and 99:1, more preferably between about 70:30 and 90:10, most preferably about 85:15. Admixing can be by conventional means. Preferably, from about 2 to 40%, by weight of the finished composition, of detergency builder is admixed with the (finished) granules.

The alkyl sulfate particles and said spray dried granules are preferably admixed with from about 3 to 10%, by weight of the finished composition, of citric acid and effective amounts of perfume and enzymes.

IV. Composition Claims

Two inventions are believed to be contained herein: the process for making the composition, and the composition itself.

- 13 -

The latter comprises alkyl sulfate particles which include from about 4 to 20% of C₁₀₋₁₆ linear alkylbenzene sulfonate and/or C₁₂₋₁₈ (coconut) soap for enhanced solubility in cold water. The alkyl sulfate is included in the high active particles rather than
5 in the base granules for the same reasons as are stated above.

Included is a granular detergent composition comprising, by weight of the finished composition:

- (a) from about 1 to 90% of alkyl sulfate particles comprising, by weight of the alkyl sulfate particles:
10 from about 60 to 99% of C₁₂₋₁₈ alkyl sulfate ethoxylated with from 0 to about 4 moles of ethylene oxide per mole of alkyl sulfate; from about 4 to 20% of C₁₀₋₁₆ linear alkylbenzene sulfonate and/or C₁₂₋₁₈ soap; and
- (b) from about 10 to 99% of base granules comprised of, by
15 weight of the granules less than about 2% alkyl sulfate, and from 0 to about 40% of anionic surfactant other than alkyl sulfate; from about 10 to 80% of detergency builder; and from about 1 to 15% of soluble silicate.

A preferred granular detergent composition herein comprises,
20 by weight of the finished composition:

- (a) from about 1 to 90% of alkyl sulfate particles consisting essentially of, by weight of the alkyl sulfate particles from about 60 to 99% of C₁₂₋₁₈ alkyl sulfate; from about 4 to 20% of C₁₀₋₁₆ linear
25 alkylbenzene sulfonate and/or C₁₂₋₁₈ soap; from about 5 to 20% of polyethylene glycol of molecular weight between about 2,000 and 50,000; from about 0.2 to 15% of an α -aminodicarboxylic acid selected from the group consisting of glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid, and 2-amino-2-methyl-pentane-
30 dioic acid, or their alkali metal salts; and from about 1 to 15% of water and/or unreacteds; and
- (b) from about 10 to 99% of base granules comprised of less than about 2% phosphorus.

35

- 14 -

The spray dried granules are preferably comprised of from 0 to about 40%, preferably about 2 to 40% of anionic surfactant other than alkyl sulfate; from about 10 to 80% of detergency builder; and from about 1 to 15% of soluble silicate.

5 The spray dried granules are preferably comprised of from about 15 to 20% of C₁₀₋₁₆ linear alkylbenzene sulfonate and from about 2 to 5% of soluble sodium silicate. The spray dried granules are also preferably comprised of from about 30 to 60 weight % of a detergency builder selected from the group
10 consisting of carbonate, citrate, aluminosilicate, and mixtures thereof. They are more preferably comprised of from about 5 to 60 weight % of sodium carbonate and/or sodium sulfate.

 The spray dried granules are preferably further comprised of from about 1 to 10% of a homopolymer or copolymer of acrylic acid
15 or its salts having an average molecular weight between about 1,000 and 10,000. The granular detergent composition herein preferably has a phosphorus content of less than about 2.0, preferably 0.

 The following are separately preferred for the alkyl sulfate particles of (a): linear alkylbenzene sulfonate range is from
20 about 6 to 12% of C₁₁₋₁₄ LAS; alkyl sulfate range is from about 65 to 90% of C₁₄₋₁₆ alkyl sulfate; polyethylene glycol range is from about 5 to 15% at a molecular weight between about 4,000 and 12,000; a-aminodicarboxylic acid salt range is from about 1 to 3%
25 and is most preferably mono- and/or disodium glutamate; and the water and/or unreacted materials range is from about 2 to 8%.

 Preferably, the ratio of LAS to alkyl sulfate is between about 60:40 and 80:20, most preferably 70:30.

 The composition preferably further comprises (admixed on top
30 of both types of granules): (c) from about 2 to 40%, preferably 5 to 15%, by weight of the finished composition, of detergency builder, or (c) from about 3 to 10%, by weight of the finished composition, of citric acid and effective amounts of perfume and enzymes. Enzymes, preferably protease, lipase and/or cellulase,
35

- 15 -

comprise less than about 3% by weight of the composition, as do perfumes.

The ratio of (a) to (b), respectively, is preferably between about 50:50 and 1:99, most preferably between about 30:70 and 10:90.

V. Optional Ingredients

Examples of detergent surfactants which can be employed herein are described in U.S. Patent 3,579,454, Collier, issued May 18, 1971, incorporated herein by reference, from Column 11, line 45 through Column 13, line 64. An extensive discussion of surfactants is contained in U.S. Patent 3,936,537, incorporated herein by reference particularly Column 11, line 39 through Column 13, line 52. Anionic synthetic surfactants are particularly preferred.

Cationic surfactants can also be included in such finished detergent compositions. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Other optional ingredients which may be included in the detergent compositions herein include detergency builders, chelating agents, bleaching agents, antitarnish and anticorrosion agents, perfume and color additives, and other optional ingredients enumerated in the Baskerville patent, U.S. Patent 3,936,537, from Column 19, line 53 through Column 21, line 21, incorporated herein by reference. Chelating agents are also described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference. Detergency builders are enumerated in the Baskerville patent from Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071,

- 16 -

Bush et al., issued May 5, 1987, both incorporated herein by reference. Such builders include, for example, phosphates, aluminosilicates, silicates, carbonates, C₁₀-C₁₈ alkyl monocarboxylates, polycarboxylates, and polyphosphonates, and mixtures thereof.

All parts, percentages and ratios used herein are by weight unless otherwise specified.

EXAMPLE I

An alkyl sulfate particle is made according to the following formula:

	<u>Weight %</u>
Sodium (C ₁₄ -15) alkyl sulfate	72.8
Sodium linear (C _{12.3}) alkyl benzene sulfonate	10.6
Water	2.0
Sodium sulfate	1.6
Polyethylene glycol (MW=8000)	8.3
Mono/disodium glutamate	2.1
Miscellaneous	2.6

Detergent compositions are made by first spray drying aqueous slurries according to the following formula:

	<u>Weight %</u>	
	<u>Product A</u>	<u>Product B</u>
	(Control)	(Test)
Sodium linear (C _{12.3}) alkyl-benzene sulfonate	14.88	15.39
Sodium (C ₁₄ -15) alkyl sulfate	6.38	0.00
Sodium carbonate	10.96	12.02
Sodium polyacrylate (MW=4500)	3.51	3.85
Sodium aluminosilicate	29.48	32.34
Sodium silicate (1.6 SiO ₂ :Na ₂ O)	2.41	2.64
Fluorescent whitening agent	0.30	0.32
Sodium sulfate	21.58	22.79
Polyethylene glycol (MW=8000)	1.62	0.99
Deaerant*	0.11	0.12

- 17 -

Moisture 8.77 9.54

*Dow Corning DC-544

Spray drying was performed in a ten foot diameter counter current spray drying tower with a single nozzle at 740 lb/hr, inlet air temperature of approximately 390°F and exhaust temperature of approximately 200°F.

Final detergent compositions are then made by admixing according to the following formula:

	Spray dried granules	91.24	83.16
10	Citric acid	5.5	5.5
	Perfume	0.30	0.34
	Protease/Amylase	0.9	0.9
	Ammonium sulfate	2	2
	Alkyl sulfate particles	0	8.01
15	Suds suppressor	0.06	0.06

** Alcalase/Rapidase (Novo)

Product A represents a control detergent composition, produced as described above. Product B is similarly produced except for the inclusion of admixed alkyl sulfate particles. It is chemically equivalent to the control.

Results

When the two laundry products described above are evaluated by consumers during a two week period in their home washing machines (single product blind test), they are rated equal.

Conclusion

The alkyl sulfate particle/spray dried granule admix allows production of laundry detergents which are chemically equivalent to current detergent compositions with no change in consumer perception. The admix provides the processing advantage of increased capacity and reduced organic emissions from the spray drying tower.

EXAMPLE II

Alkyl sulfate particles as described in Example I can be used in the following detergent formulation.

- 18 -

		<u>Weight %</u>	
		<u>Product C</u>	<u>Product D</u>
		(Control)	(Test)
5	Sodium linear (C ₁₂₋₃) alkyl- benzene sulfonate	9.70	8.29
	Sodium (C ₁₄₋₁₅) alkyl sulfate	9.70	0.00
	Sodium carbonate	10	10
	Sodium polyacrylate (MW 4500)	3.2	3.2
	Sodium aluminosilicate	26.9	26.9
10	Sodium silicate (1.6 SiO ₂ :Na ₂ O)	2.2	2.2
	Fluorescent whitening agent	0.27	0.27
	Sodium sulfate	19.69	18.82
	Polyethylene glycol (MW=8000)	1.48	0.37
	Deaerant*	0.1	0.1
15	Moisture	8.	7.73
	<u>Admixed</u>		
	Citric acid	5.5	5.5
	Perfume	0.30	0.34
	Protease/Amylase	0.9	0.9
20	Ammonium sulfate	2	2
	Alkyl sulfate particle	0	13.32
	Suds suppressor	0.06	0.06

*Dow Corning DC-544

** Alcalase/Rapidase (Novo)

25 These formulae are again chemically equivalent to each other.
 Product C, the control, is the same as Product A, the control in
 Example I, except the ratio of the surfactants alkyl
 sulfate:linear alkylbenzene sulfonate is changed from 30:70 to
 50:50. Product C is no longer manufacturable by spray drying due
 30 to environmental constraints on the residual organics introduced
 to the spray drying tower by the additional alkyl sulfate.
 However, Product D can be produced with less environmental impact
 than even Product A. Product D would be expected to perform

- 19 -

better in contexts where alkyl sulfate is the preferred surfactant.

EXAMPLE III

Alkyl sulfate particles as described in Example I can be used
5 in the following detergent formulations:

		<u>Weight %</u>	
		<u>Product E</u>	<u>Product F</u>
		(Control)	(Test)
10	Sodium linear (C _{12.3}) alkyl-benzene sulfonate	19.09	17.90
	Sodium (C ₁₄₋₁₅) alkyl sulfate	8.18	0
	Sodium carbonate	10	10
	Sodium polyacrylate (MW 4500)	3.2	3.2
	Sodium aluminosilicate	26.9	26.9
15	Sodium silicate (1.6 SiO ₂ :Na ₂ O)	2.2	2.2
	Fluorescent whitening agent	0.27	0.27
	Sodium sulfate	11.82	11.06
	Polyethylene glycol (MW=8000)	1.48	0.55
	Deaerant*	0.1	0.1
20	Moisture	8.	7.78
	<u>Admixed</u>		
	Citric acid	5.5	5.5
	Perfume	0.30	0.34
	Protease/Amylase	0.9	0.9
25	Ammonium sulfate	2	2
	Alkyl sulfate particles	0	11.24
	Suds suppressor	0.06	0.06

*Dow Corning DC-544

** Alcalase/Rapidase (Novo)

30 These formulae are chemically equivalent to each other. Product E, the control, is the same as Product A, the control in Example I, except the total surfactant (linear alkylbenzene sulfonate plus alkyl sulfate) in the formula is increased from 19.40% to 27.27%. Product E can no longer be manufactured by

35

- 20 -

spray drying for reasons of safety and environmental impact and because the physical properties of the spray dried granules would be expected to be poor (i.e. lumping and caking). However, Product F is manufacturable by the combination of spray drying and admixing of alkyl sulfate particles. This product would be expected to perform better than Product A on surfactant sensitive soils.

EXAMPLE IV

The following detergent compositions are made on a ten-foot diameter counter current spray drying tower:

	<u>Control</u>	<u>Test</u>
Sodium C _{12.3} alkylbenzene sulfonate	11.45	11.27
Sodium C _{14.5} alkyl sulfate	11.45	0
Sodium aluminosilicate (hydrated, 20% water)	28.90	28.90
Sodium carbonate	17.00	17.00
Sodium silicate (1.6 SiO ₂ :Na ₂ O)	5.35	5.35
Sodium polyacrylate (MW=4500)	3.5	3.5
Polyethylene glycol (MW=8000)	1.2	0
Fluorescent whitening agent	0.22	0.22
Tallow fatty acid	1.28	1.28
Water, sodium sulfate	rest	rest
<u>Cake Grade Results:</u>		
Force (lbs/in ²) to break cake under 20 lb load	5.2	2.3
Water by analysis	11.4	11.1

The improved physical property (lower cake grade) of the test product demonstrates the advantage of minimizing the surfactant content of spray dried granules. This is true even though the crispening aid, polyethylene glycol (MW=8000), is removed along with the most crisp surfactant, alkyl sulfate.

EXAMPLE V

Preparation of high active detergent material suitable for granulation to a free flowing particulate is as follows.

35

- 21 -

Equipment

A falling film SO_3 reactor is used to prepare the acid form of C_{14-15} alkyl sulfate. The acid is fed to a high active neutralization system supplied by Chemithon Corporation of Seattle, Washington. This customized neutralization system consists of a recycle loop containing a heat exchanger for cooling, a recirculation pump suitable for highly viscous fluids, and a high shear mixer with which the reactants are introduced.

In order to attain the very low moisture levels necessary for a free-flowing, high active particles, the neutralization loop is modified to handle 70% sodium hydroxide melt rather than the 38-50% normally used with the neutralization loop. The modification consists of hot water jackets and electrical heating of the caustic feed system to maintain the 70% caustic above the caustic melting point of about 155°F (68.3°C).

Another necessary modification is the addition of a metering system which injects the polyethylene glycol into the neutralization loop at the discharge side of the high shear mixer. The presence of the polyethylene glycol facilitates pumping of the paste in the recirculation loop and reduces stickiness of the finished material. Polyethylene glycol having a molecular weight of about 8000 is added as a melt (about 160°F or 71.1°C) at a rate of about 1 part polyethylene glycol 8000 to 10 parts C_{14-15} sodium alkyl sulfate active.

Operation

At start up, the neutralization loop is filled with water and the system is maintained at $180-230^\circ\text{F}$ ($82.2-110^\circ\text{C}$) by using hot water in the heat exchanger and in the double wall pipe comprising the recycle loop. The recycle pump and high shear mixer are started.

The 70% sodium hydroxide and C_{14-15} alkyl sulfuric acid are introduced into the high shear mixer and allowed to react. The sodium hydroxide and C_{14-15} alkyl sulfuric acid are metered to allow a slight excess of sodium hydroxide. Material displaced

35

- 22 -

from the recirculation loop is discharged through a back pressure control valve.

As operation continues, the water is displaced from the loop and the concentration of the sodium C₁₄₋₁₅ alkyl sulfate is increased to over 70% active. Operation is continued until the desired amount of high active, low moisture material is produced. The reactant feed is then shut off and the reaction loop is washed with hot water.

Results

The molten paste produced is cooled and manually ground to a free-flowing particulate product having the following composition.

Sodium C ₁₄₋₁₅ alkyl sulfate	74.9%
Polyethylene glycol 8000	8.5
Water	9.1
Sodium hydroxide	0.6
Unreactants/miscellaneous	6.9

EXAMPLE VI

An alkyl sulfate particle is made according to the following formula:

	<u>Nominal Wt%</u>
Sodium (C ₁₄₋₁₅) alkyl sulfate	75.0
Water	11.0
Sodium sulfate	2.5
Polyethylene glycol (MW=8000)	7.5
Miscellaneous	4.0

Detergent compositions are made by first spray drying aqueous slurries according to the following formula:

	<u>Weight %</u>	
	<u>Product A</u>	<u>Product B</u>
	(Control)	(Test)
Sodium linear (C _{12.3}) alkyl-benzene sulfonate	11.90	13.25
Sodium (C ₁₄₋₁₅) alkyl sulfate	11.02	0.00
Sodium carbonate	18.21	18.87

- 23 -

	Sodium polyacrylate (MW=4500)	3.34	4.12
	Sodium aluminosilicate	23.39	31.40
	Sodium silicate (1.6 SiO ₂ :Na ₂ O)	1.82	1.90
	Fluorescent whitening agent	0.31	0.28
5	Sodium sulfate	15.08	20.94
	Polyethylene glycol (MW=8000)	0.94	0.32
	Sodium tallow sope	1.03	1.36
	Moisture	7.96	7.56

10 Spray drying is performed in a ten foot diameter counter current spray drying tower with a single nozzle at 740 lb/hr, inlet air temperature of approximately 390°F and exhaust temperature of approximately 200°F.

Final detergent compositions are then made by admixing according to the following formula:

15	Spray dried granules	100.00	84.37
	Alkyl sulfate particle	0	15.63

20 Product A represents a control detergent composition, produced as described above. Product B is similarly produced except for the inclusion of admixed alkyl sulfate particle. It is chemically equivalent to the control.

Conclusion

25 The alkyl sulfate particle/spray dried granule admix allows production of laundry detergents which are chemically equivalent to current detergent compositions. The admix provides the processing advantages of increased capacity and reduced organic emissions from the spray drying tower.

30

WHAT IS CLAIMED IS:

1. A process for the production of a granular detergent composition, comprising:
 - (a) spray drying a slurry comprising, by weight of the spray dried granules: less than 2% of alkyl sulfate; from 0 to 40% of anionic surfactant other than alkyl sulfate; from 10 to 80%, preferably 2 to 40%, of detergency builder; and from 1 to 15% of soluble silicate;
 - (b) producing alkyl sulfate particles by steps comprising high active continuous neutralization, said particles comprising, by weight of the alkyl sulfate particles: from 60 to 99% of C₁₂₋₁₈ alkyl sulfate ethoxylated with from 0 to 4 moles of ethylene oxide per mole of alkyl sulfate; and
 - (c) admixing said spray dried granules with said alkyl sulfate particles in a ratio between 10:90 and 99:1.
2. A process according to Claim 1 wherein said anionic surfactant in said spray dried granules is a salt of C₁₀₋₁₆ linear alkylbenzene sulfonate.
3. A process according to Claim 1 or 2 wherein said spray dried granules are comprised of from 30 to 60 weight % of a detergency builder selected from the group consisting of carbonate, citrate, aluminosilicate, and mixtures thereof.
4. A process according to any of the preceding claims wherein said spray dried granules are comprised of from 5 to 50 weight % of sodium aluminosilicate; and from 5 to 60 weight % of sodium carbonate and/or water-soluble inorganic salt.
5. A process according to any of the preceding claims wherein said slurry further comprises from 2 to 5% of soluble sodium silicate.
6. A process according to any of the preceding claims wherein said high active continuous neutralization is conducted by a process comprising the steps of:

- (a) reacting in a continuous neutralization system C₁₂₋₁₈ alkyl sulfuric acid with a sodium hydroxide solution, which is greater than or equal to 62% by weight of the hydroxide, to produce a neutralized product;
 - (b) adding to said continuous neutralization system during formation of said neutralized product, polyethylene glycol of a molecular weight between 2,000 and 50,000; ethoxylated nonionic surfactant of the formula $R(OC_2H_4)_nOH$, wherein R is a C₁₂₋₁₈ alkyl group or a C₈₋₁₆ alkyl phenol group and n is from 9 to 80, with a melting point of greater than or equal to 120°F (48.9°C); or mixtures thereof;
- wherein the weight ratio of the additive of step (b) to the product of step (a) is from 1:5 to 1:20.

7. A process according to any of the preceding claims wherein C₁₀₋₁₆ linear alkylbenzene sulfonic acid is also added to said continuous neutralization system, such that said alkyl sulfate particles contain from 4 to 25% of C₁₀₋₁₆ linear alkylbenzene sulfonate.

8. A process according to any of the preceding claims wherein the materials of the detergent composition are not kneaded in the continuous neutralization system; and wherein said continuous neutralization system is substantially free of additional crude materials, and does not include an airtight-type kneader.

9. A process according to any of the preceding claims wherein essentially no detergency builders or additional organic materials are fed into said continuous neutralization system.

10. A process according to any of the preceding claims wherein said neutralized product has less than or equal to 12% by weight of water; and said continuous neutralization system is a

continuous neutralization loop; and said additive of step (b) is polyethylene glycol of a molecular weight between 3,000 and 20,000; and said weight ratio of the additive of step (b) to the product of step (a) is 1:10.

11. A process according to any of the preceding claims wherein said additive of step (b) is molten polyethylene glycol with a molecular weight of 8,000.

12. A process according to any of the preceding claims wherein R is a C₁₂₋₁₈ alkyl group and n is from 12 to 30.

13. A process according to any of the preceding claims wherein said high active continuous neutralization is conducted by a process comprising the steps of:

- (a) reacting in a high active continuous neutralization loop the acid form of said alkyl sulfate with sodium hydroxide solution, which is 30 to 75% by weight of the hydroxide and is present in stoichiometric amount to slight stoichiometric excess, to produce a neutralized product;
- (b) adding to said continuous high active neutralization loop, during formation of said neutralized product, an α -aminodicarboxylic acid selected from the group consisting of glutamic acid, aspartic acid, aminomalonic acid, aminoadipic acid, and 2-amino-2-methyl-pentanedioic acid, or their alkali metal salts, such that particles formed from the product of step (b) are comprised of from 0.2 to 15 weight % of the α -aminodicarboxylic acid salt.

14. A process according to any of the preceding claims wherein an alkali metal salt of glutamic acid or aspartic acid is added to

said neutralization loop; and said alkali metal hydroxide solution is 62 to 73% by weight of the hydroxide.

15. A process according to any of the preceding claims wherein from 1 to 10 weight % mono- or disodium glutamate is added to the neutralization loop; and said alkali metal hydroxide solution is sodium hydroxide.

16. A process according to any of the preceding claims comprising the additional step of adding to the neutralization loop during formation of said neutralized product, polyethylene glycol of a molecular weight between 2,000 and 50,000; ethoxylated nonionic surfactant of the formula $R(OC_2H_4)_nOH$, wherein R is a C_{12-18} alkyl group or a C_8-16 alkyl phenol group and n is from 9 to 80, with a melting point of greater than or equal to 120°F (48.9°C); or mixtures thereof in a weight ratio of from 1:5 to 1:20 with the ingredients of step (a).

17. A process according to any of the preceding claims wherein said polyethylene glycol has a molecular weight of 8000 and the weight ratio of said polyethylene glycol to the ingredients of step (a) is 1:10.

18. A process according to any of the preceding claims further comprising simultaneously cooling and extruding the molten neutralized product, and cutting or grinding into detergent particles.

19. A process according to any of the preceding claims further comprising cooling said product of step (b) on a chill roll until it has solidified, and flaking said solidified product off said chill roll into detergent flakes, drying to below 5% moisture, and mechanically grinding into detergent particles.

20. A process according to any of the preceding claims wherein said alkyl sulfate particles are comprised of from 70 to 90% of sodium C₁₄₋₁₆ alkyl sulfate.

21. A process according to any of the preceding claims wherein the phosphorus content of said granular detergent composition is less than 2.0%.

22. A process according to any of the preceding claims comprising admixing with said alkyl sulfate particles and said spray dried granules from 3 to 10%, by weight of the finished composition, of citric acid and effective amounts of perfume and enzymes; and said ratio of alkyl sulfate particles to spray dried granules is between 30:70 and 10:90, respectively.

INTERNATIONAL SEARCH REPORT

PCT/US 92/05659

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C11D1/14; C11D17/06; C11D11/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	US,A,5 066 425 (K. OFOSU-ASANTE ET AL.) 19 November 1991 cited in the application see column 7, line 23 - column 8, line 55; claims 1-5,10,14,15 ---	1,2,6, 10-21
X	EP,A,0 402 112 (PROCTER & GAMBLE) 12 December 1990 see page 6, line 35 - page 7, line 24; claims ---	1,2,6, 10-21
Y	& US,P,364 721 cited in the application ---	1-21
Y	US,A,4 075 117 (E.J. MORTON ET AL.) 21 February 1978 see the whole document ---	1-21
	-/--	
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 DECEMBER 1992	- 8. 12. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	GRITTERN A.G.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 084 657 (HENKEL) 3 August 1983 see page 3, line 29 - page 5, line 25 see page 11, line 1 - line 9 ----	1-5
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 77-58548Y & JP,A,52 080 309 (LION FAT & OIL KK) see abstract -----	1,3

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9205659
SA 62103

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 03/12/92

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-5066425	19-11-91	AU-A-	8418591	18-02-92
		CN-A-	1059366	11-03-92
		WO-A-	9201778	06-02-92

EP-A-0402112	12-12-90	AU-A-	5696590	13-12-90
		CA-A-	2017922	09-12-90
		CN-A-	1048408	09-01-91
		JP-A-	3072600	27-03-91
		US-A-	5152932	06-10-92

US-A-4075117	21-02-78	None		

EP-A-0084657	03-08-83	DE-A-	3151536	07-07-83
		US-A-	4524010	18-06-85

EPO FORM P0079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)